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In re Application of: Donald A. Meltzer et al.

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Title: THERMOPLASTIC POLYURETHANES

Honorable Commissioner for Patents
U.S. Patent & Trademark Office
P.O. Box 1450
Alexandria, Virginia 22313-1450

Dear Sirs:

DECLARATION UNDER 37 C.F.R. §1.132

I, Donald A. Meltzer, declare as follows:

I received a Bachelor of Science degree with a major in chemistry in 1985 from McGill University. I received a PhD in Polymer Science and Engineering in 1990 from the University of Massachusetts. I have been employed by The Lubrizol Corporation since 1996 in various roles. In my current role I am involved in the development and formulation of thermoplastic polyurethanes (TPUs) for various applications including such things as breathable films, conveyor belts, wood press belts, flexible storage containers, hot melt adhesives, printing blankets and polishing pads.

I am an inventor of the present application and familiar with the subject matter of the present application and the references cited against it.

CERTIFICATE OF EFS SUBMISSION (37 C.F.R. § 1.8(a)(1)(C))

I hereby certify that this correspondence is being filed electronically via the USPTO EFS to the Commissioner for Patents, United States Patent & Trademark Office, in accordance with §1.6(a)(4) on:

July 8, 2010
Date of Deposit

/ Cathy Bartel /
Deposited by: Cathy Bartel

The present invention concerns improved thermoplastic polyurethane (TPU) compositions. We have found that TPU compositions prepared from a polyester polyol used in combination with a polyether co-polyol, specifically poly(tetramethylene ether) glycol (PTMEG), and symmetrical chain extenders used in combination with a co-chain extender, provide significantly improved properties over TPU compositions missing the polyether co-polyol, the co-chain extender, or both. The combination of these various features provides the improved performance.

The examples in the specification filed in this case show the improved performance the compositions of interest provide, specifically Tables 1 and 2. Table I below summarizes the examples from Tables 1 and 2 in the specification that use 1,3-butanediol (1,3-BDO) as the chain extender. Table II below summarizes the examples from Tables 1 and 2 in the specification that use dipropylene glycol (DPG) as the chain extender. The comparative examples that do not contain any co-chain extender have been included in both tables. The examples have been reordered so that comparative and invention examples are now grouped together but use the same ID numbers.

The physical and rheological properties presented in the table are described in greater detail in the specification but generally deal with the re-crystallization and/or solidification properties of the material being tested. For each of the rheological properties tested below, a lower value is desirable and, for the purposes of this invention, indicates improved performance.

Furthermore, it is also desirable to achieve a balance between these physical and rheological properties and the desired Tg. Tg tends to increase with the use of a co-chain extender. One aspect of the present invention is to achieve the desired physical and rheological properties while also maintaining a sub-ambient Tg.

In addition, it can be seen that the use of a co-chain extender can have the undesired effect of increasing certain properties, particularly the $V_f(T_m+35)$, $V_f(T_m+15)$ and $V_{ff}((T_m+15)/(T_m+35))$ values, as demonstrated by the examples in the tables below. The presence of a co-chain extender in compositions where the $V_f(T_m+35)$, $V_f(T_m+15)$ and $V_{ff}((T_m+15)/(T_m+35))$ values do not increase to the level seen in the comparative examples that contain co-chain extenders is also a positive result of the present invention.

TABLE I – Examples Containing 1,3-BDO

EXAMPLE ID	CO-CHAIN EXT	CO-POLYOL	CO-CHAIN EXT TO CO-POLYOL RATIO	PHYSICAL & RHEOLOGICAL PROPERTIES						
				Tc	T _{CN}	Tg	V _f (T _m +15)	V _{ff} ((T _m +15)/(T _m +35))	V _f (T _m +35)	
Comp 1	YES	NO	-	76	0.90	-14	15	17	7.3	1.2
Comp 4	YES	NO	-	78	0.93	-17	12	26	4.1	4.5
Comp 6	NO	YES	0	76	0.90	-17	6	9	3.0	4.9
Comp 7	NO	YES	0	75	0.89	-20	5	8	2.2	4.7
Comp 15	NO	NO	-	84	1.00	-15	7	13	3.3	4.8
Inv 2	YES	YES	1.0	67	0.80	-9	4	6	2.4	1.8
Inv 3	YES	YES	0.5	67	0.80	-9	6	7	3.2	1.4
Inv 5	YES	YES	0.5	67	0.80	-10	4	6	2.2	2.9
Inv 13	YES	YES	0.65	76	0.90	-16	6	8	3.5	1.5
Inv 14	YES	YES	0.25	73	0.87	-12	5	8	3.1	2.2
Inv 16	YES	YES	0.65	79	0.94	-15	5	9	2.4	3.1

Each of the inventive examples summarized in the table above improves at least one of the physical and rheological properties and in most cases several properties. For instance, Inventive Examples 2 and 5 exhibits a T_c, a T_{CN}, a V_f(T_m+15) and a V_{ff}((T_m+15)/(T_m+35)) lower than the values that any of the comparative examples provide. Inventive Examples 13 and 16 exhibit values for several physical and rheological properties at the bottom of the range that can be achieved by the comparative examples while also exhibiting a V_f(T_m+15), a V_{ff}((T_m+15)/(T_m+35)), and a V_f(T_m+35) lower than any of the co-chain extender-containing comparative examples. In addition, all of the inventive examples in Table I exhibit lower V_f(T_m+15), V_{ff}((T_m+15)/(T_m+35)), and V_f(T_m+35) values than any of the co-chain extender-containing comparative examples in the table.

TABLE II – Examples Containing DPG

EXAMPLE ID	CO-CHAIN EXT	CO-POLYOL	CO-CHAIN EXT TO CO-POLYOL RATIO	PHYSICAL & RHEOLOGICAL PROPERTIES						
				Tc	T _{CN}	Tg	V _f (T _m +15)	V _{ff} ((T _m +15)/(T _m +35))	V _f (T _m +35)	
Comp 6	NO	YES	0	76	0.90	-17	6	9	3.0	4.9
Comp 7	NO	YES	0	75	0.89	-20	5	8	2.2	4.7
Comp 8	YES	NO	-	84	1.00	-12	6	10	3.4	2.4
Comp 11	YES	NO	-	77	0.92	-15	6	10	2.2	4.4
Comp 15	NO	NO	-	84	1.00	-15	7	13	3.3	4.8
Inv 9	YES	YES	1.0	75	0.89	-14	4	8	2.2	2.1
Inv 10	YES	YES	0.5	74	0.88	-12	5	7	2.3	3.3
Inv 12	YES	YES	0.50	74	0.88	-11	6	9	3.6	3.1

Each of the inventive examples summarized in the table above improves at least one of the physical and rheological properties and in most cases several properties. For instance, Inventive Examples 10 and 12 exhibit T_c and T_{cn} values lower than any of the comparative examples. Inventive Example 9 exhibits a V_f(T_m+15) and a V_t value lower than any of the comparative examples. In addition, all of the inventive examples in Table II exhibit lower V_f(T_m+15) and V_{f1}((T_m+15)/(T_m+35)) values than any of the co-chain extender-containing comparative examples in the table.

These results indicate the inventive examples represent significant improvements in the physical and rheological properties of the TPU compositions involved, making them much more suited for specific applications including fabrics, films and coatings and most particularly, conveyor belts, wood press belts, flexible storage containers, and printing blankets.

In addition to the results summarized above, I also provide some additional data that further demonstrates the benefits of the compositions of this invention over more conventional compositions, specifically the benefits of using PTMEG over other co-polyols when also using the chain extenders and co-chain extenders of the present invention. Two TPU compositions were prepared and then tested to demonstrate their physical properties including abrasion resistance, an important performance parameter for many applications such as coatings.

Inventive Example A was prepared according to the present invention, using the methods described in the application. The formulation of Example A includes 151 pbw polybutylene adipate, 23 pbw PTMEG, 24 pbw 1,4-BDO and 2 pbw 1,3-BDO where the PTMEG is the co-polyol and the 1,3-BDO is the co-chain extender.

Comparative Example B was prepared according to the present invention, using the methods described in the application except that it does not contain PTMEG, but rather a different co-polyol, Poly G 55-112 (a commercially available 1000 MW poly(oxyethylene-co-oxypropylene) diol having an EO content of about 50 percent by weight). The formulation of Example B includes 146 pbw polybutylene adipate, 26 pbw Poly G 55-112, 24 pbw 1,4-BDO and 2 pbw 1,3-BDO where the Poly G 55-112 is the co-polyol and the 1,3-BDO is the co-chain extender.

Table II below summarizes the test results collected on these two examples.

TABLE II

TEST RESULTS		EXAMPLE A	EXAMPLE B	TEST METHOD
Ult. Tensile	psi	5540	7100	ASTM D412-98
Ult. Elongation	%	508	525	ASTM D412-98
Stress at 50%	psi	1110	1140	ASTM D412-98
Stress at 100%	psi	2650	1270	ASTM D412-98
Stress at 300%	psi	4000	2410	ASTM D412-98
Graves Tear: Die C	lb/in	616	560	ASTM D624-00
Trouser Tear	lb/in	168	180	ASTM D470-95
Specific Gravity		1.20	1.21	ASTM D792-98A
Hardness (5 sec)	A/D	91.3 (A)	93(A)	ASTM D2240-00
Tensile Set (200%)	%	23	26	ASTM D412-98
Compression Set (25%, 23C)	%	29	23	ASTM D395-98
Taber Abrasion (H18, 1000g)	Mg/1000 cycles	30	70	ASTM D3389-99

The results show the benefits of the present invention, particularly in the abrasion testing. For the Taber Abrasion test, a lower test result indicates lower levels of abrasive damage, which indicates better abrasion resistance. Inventive Example A has a Taber Abrasion result less than half the value obtained by Comparative Example B, indicating a very significant improvement over the comparative example.

As indicated by the results above, when the various features of the invention are used in combination, specifically when TPU compositions are prepared from a polyester polyol used in combination with a polyether co-polyol, specifically poly(tetramethylene ether glycol) (PTMEG), and symmetrical chain extenders used in combination with a co-chain extender, they provide significantly physical properties over TPU compositions that are missing the polyether co-polyol, the co-chain extender, or both.

Based on these results, I expect these improved results to be present whenever any of the chain extenders and co-extenders specified by the claims are used, at least as long as the other parameters of the claims are met.

I further declare that all statements herein made of my own knowledge are true and all statements herein made on information and belief are believed to be true. I understand that willful false statements and the like are punishable by fine or imprisonment or both (18 U.S.C. 1001) and may jeopardize the validity of the application or any patent issuing thereon.


Donald A. Meltzer

June 14, 2010
Date